

# Mechanism of dehydration and intumescence of soluble silicates

## Part II *Effect of the cation*

K. B. LANGILLE, D. NGUYEN, J. O. BERNT

*Dacto Technology Limited, Mississauga, Ontario, Canada*

D. E. VEINOT

*Defence Research Establishment Atlantic, Halifax, Nova Scotia, Canada*

M. K. MURTHY

*MKM International, Toronto, Ontario, Canada*

The effect of the cation present in soluble silicates was investigated by studying the properties of lithium, sodium, and potassium silicates by thermal analysis, X-ray diffraction, and water absorption tests. Intumescence and solubility of the samples were found to be dependent on the strength of cationic cross-links between polysilicate particles. The degree of intumescence and solubility both decrease in the order  $K^+ > Na^+ > Li^+$ . Ionic hydration was found to be the primary mechanism for the water absorption of the silicate samples.  $Si_2O_5^{2-}$  crystalline regions were found to exist in potassium and lithium silicate samples.

### 1. Introduction

Soluble silicates have long been proposed as the vehicle for inorganic fire protective coatings owing to their property of intumescence (swelling) when exposed to flame. However, this technology has yet to be exploited commercially due primarily to the hygroscopic nature of soluble silicates which causes ageing after prolonged exposure to atmospheric conditions. Related to this hygroscopic nature is the poor water resistance of such coatings. Thus, understanding the nature of the water retained in the silicate-based coatings, and what factors affect it, will be useful in the development of such coatings.

Numerous patents exist which use either individually or jointly lithium, sodium and potassium silicates as the vehicle in fire protective coatings [1-4]. Depending on the cation present (i.e. lithium, sodium or potassium) the coatings will possess different properties with respect to both hygroscopic nature and intumescence. This study is concerned with the effect of the different cations on the retained water and intumescence.

Thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and X-ray diffraction (XRD) were used to give direct information on the nature of retained water, and physical structure of the silicate material. In addition, water solubility, intumescence (i.e. upon exposure to flame), and water absorption–relative humidity tests give indirect evidence of the physical structure, and nature of water bonding in the silicate-based coatings.

### 2. Background

#### 2.1. Nature of cations in the silicate structure

Soluble silicates form a complex constitution in aque-

ous solution consisting of polysilicate ions varying from a few  $-O-Si-O-$  units to several depending on the concentration and silica:metal oxide molar ratio [5-8]. These polysilicate ions are in equilibrium with mononuclear molecules (i.e.  $Si(OH)_4$  and its ions  $(SiO(OH)_3)^-$  and  $(SiO_2(OH)_2)^{2-}$ ).

Upon drying, the cations in solution would act as cross-links between polysilicate particles through coordination with negatively charged polysilicate oxygen atoms (surface  $-SiO^{-1}$  groups) [6, 9]. In the case of monovalent ions, such linkages would be broken due to dissociation upon submersion of such a sample in water. The rate of dissolution would depend on the strength of cross-links between particles. In the case of multivalent cations, such as  $Ca^{2+}$ , strong bonds link adjacent silicate particles and form insoluble precipitates when added to a silicate solution.

Intumescence takes place as water vapour is rapidly evolved from the silicate coating upon exposure to heat. In order for the coating to intumesce, the silicate structure must be capable of expanding by the silicate matrix being forced apart. Thus, the strength of bonding between polysilicate ions should have a definite effect on the degree of intumescence.

#### 2.2. Nature of silicate-bound water

The water contained by a room-dried silicate sample can be considered to consist of "free" water and "bound" water as discussed in a previous paper [10].

The bound water is that given off at higher temperatures and includes, (1) water hydrogen-bonded to surface silanol groups of silica particles (polysilicate ions) [11-13], (2) ionic hydration (i.e. water molecules associated with each of the cations and negatively

charged polysilicate ions), and (3) water present as SiOH groups on the polysilicate ions which is released at high temperatures [14, 15]. Only ionic hydration is directly affected by replacing the cation present in the silicate coating.

For the case of ionic hydration, it is known that in aqueous solution water molecules are associated with each cation. The number of water molecules bound to a particular cation (i.e. hydration number) depends on the ionic radius, the number decreasing with increasing ionic radius.  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{K}^+$  have hydration numbers of 4, 3 and 2, respectively [16, 17]. Different methods of analysis give roughly concordant values for the hydration number. Upon drying, this water associated with the ions may fit into the ionic lattice to form hydrates.

The number of water molecules associated with the cations in solution is usually different from that of the hydrated ionic compound because this number depends on the electrostatic equilibrium developed between cation, anion and water molecules which is determined by a number of factors including the size and charge of the cation and anion [18]. Several of the known hydrates of lithium-, sodium-, and potassium-silicate are listed in Table I [5, 19]. Some of these are not true hydrates in the sense that the water molecules fit in between the ionic lattice but instead contain structural water (i.e. that water present as  $-\text{OH}$  groups which is released at relatively high temperatures). Others contain both types of water. The crystal structures of the so-called sodium metasilicate hydrates,  $\text{Na}_2\text{SiO}_3 \cdot n\text{H}_2\text{O}$ , all in fact contain  $\text{H}_2\text{SiO}_4^{2-}$  ions and should be written as  $\text{Na}_2\text{H}_2\text{SiO}_4 \cdot (n-1)\text{H}_2\text{O}$ . They should properly be called "dihydrogen orthosilicates" as written in Table I and contain both structural water and ionic crystal lattice water [8]. Some of the listed hydrates are probably present in the dried soluble silicate samples but hydrates of higher order silicates, including irregular polysilicate ions, are expected to be predominant in the relatively high silica:metal oxide molar ratio samples which were studied.

TABLE I Alkali silicate hydrates

Formula	Systematic name
$\text{Li}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$	Dilithium disilicate dihydrate
$\text{Li}_3[\text{SiO}_3(\text{OH})]$	Trilithium hydrogen orthosilicate
$\text{Li}_4[\text{Si}_2\text{O}_5(\text{OH})_2]$	Tetalithium dihydrogen disilicate
$\text{Na}_2\text{SiO}_2(\text{OH})_2 \cdot n\text{H}_2\text{O}$	Disodium dihydrogen orthosilicate hydrates $n = 4, 5, 7, 8$
$\text{NaSi}_2\text{O}_3(\text{OH})_3 \cdot \text{H}_2\text{O}$	Sodium trihydrogen disilicate monohydrate
$\text{KSi}_2\text{O}_4(\text{OH})$	Potassium hydrogen disilicate

### 3. Experimental details

#### 3.1. Preparation of silicate solutions

##### 3.1.1. Preparation of potassium-sodium silicate solutions

The starting potassium silicate solution was PQ Corporation Kasil no. 6. This has an  $\text{SiO}_2:\text{K}_2\text{O}$  molar ratio of 3.29 with 12.65 wt %  $\text{K}_2\text{O}$  and 26.50 wt %  $\text{SiO}_2$  in aqueous solution.

The starting sodium silicate solution was PQ Corporation Sodium Silicate "N" with an  $\text{SiO}_2:\text{Na}_2\text{O}$  molar ratio of 3.33 with 8.90 wt %  $\text{Na}_2\text{O}$  and 28.7 wt %  $\text{SiO}_2$  in aqueous solution. Because these experiments were designed to investigate the cationic effect, the sodium silicate was selected to have approximately the same silica:metal oxide molar ratio as the potassium silicate in order to eliminate molar ratio effects.

Five solutions consisting of 100 wt % potassium silicate, 75 wt % potassium silicate/25 wt % sodium silicate, 50 wt % potassium silicate/50 wt % sodium silicate, 25 wt % potassium silicate/75 wt % sodium silicate, and 100 wt % sodium silicate were prepared.

##### 3.1.2. Preparation of potassium-lithium silicate solutions

The starting lithium silicate solution was DuPont Polysilicate 48 with an  $\text{SiO}_2:\text{Li}_2\text{O}$  molar ratio of 5.0 with 20.0 wt % silica and 2.1 wt %  $\text{Li}_2\text{O}$  in aqueous solution. This molar ratio was too high for our purposes because it forms an extremely brittle coating if applied to aluminium. Therefore, the molar ratio was reduced to 3.4 (to be the same molar ratio as Kasil no. 88) by adding the appropriate amount of lithium hydroxide monohydrate ( $\text{LiOH} \cdot \text{H}_2\text{O}$ , purified).

The potassium silicate selected was PQ Corporation Kasil no. 88 with an  $\text{SiO}_2:\text{K}_2\text{O}$  molar ratio of 3.45, 9.05 wt %  $\text{K}_2\text{O}$  and 19.9 wt %  $\text{SiO}_2$  in aqueous solution. This solution was selected because the silica solids content was close to that of the polysilicate 48 solution.

Five solutions consisting of 100 wt % potassium silicate, 75 wt % potassium silicate/25 wt % lithium silicate, 50 wt % potassium silicate/50 wt % lithium silicate, 25 wt % potassium silicate/75 wt % lithium silicate, and 100 wt % lithium silicate were prepared.

#### 3.2. TGA studies

Samples of the prepared solutions were allowed to room dry for 1 wk and then sealed in plastic bags until testing. These samples were then analysed thermogravimetrically using a DuPont 951 analyser. The TGA heating rate was controlled at  $5^\circ\text{C min}^{-1}$  over the temperature range of 25 to  $200^\circ\text{C}$  and  $10^\circ\text{C min}^{-1}$  over the range 200 to  $700^\circ\text{C}$ . The weight loss is a direct result of the evolution of water because no combustibles are present in the samples.

#### 3.3. DSC studies

Portions of samples prepared for the TGA studies were used for the DSC studies. Tests were performed on a Perkin-Elmer DSC-2 at a heating rate of  $5^\circ\text{C min}^{-1}$  over the temperature range 30 to  $500^\circ\text{C}$ . Samples were contained in sealed aluminium sample dishes which were perforated with a pin to allow water vapour to escape. This was necessary because a build-up of vapour pressure would affect the onset of an

endotherm. However, due to the loss of water vapour an accurate determination of the change in enthalpy could not be determined.

### 3.4. Water absorption tests

The purpose of this test was to determine expansion due to water absorption, and water retention of the silicate-based coatings at various relative humidities.

One coated aluminium sample and two petri dish samples of each composition were placed in a humidity chamber at 22 °C and the relative humidity varied using sulphuric acid-water solutions in accordance with ASTM E104-85 [20].

The aluminium samples were coated with the silicate solutions to a dried film thickness of 0.5 to 1 mm to be used for expansion tests. The thickness of the applied coating on each aluminium substrate sample was measured at three different marked locations using a digital micrometer accurate to 0.001 mm. Each subsequent measurement was taken at the same points to ensure consistency.

The petri dish samples were included in the test to give an indication of per cent water retained versus relative humidity. Solution (5 g) was introduced into each petri dish and allowed to room dry for a period of 1 wk.

The samples were tested at relative humidities of 5%, 25%, 57%, 82% and 95%, starting at 5% r.h. The samples were allowed to equilibrate before increasing the relative humidity. This was checked by weighing samples daily until the weight was constant.

### 3.5. Solubility tests

Solubility was determined by submerging petri dish (4 cm diameter) samples of each composition into individual trays of 500 ml distilled water at 22 °C for

1 h. The water was stirred manually every 5 min. After 1 h the petri dishes were removed and allowed to dry overnight before weighing to determine weight loss.

### 3.6. Intumescence tests

Degree of intumescence was determined using a fire test apparatus as described in a previous paper [10]. Coated aluminium samples from each composition were used in this test. These samples had been room dried for a period of 1 wk.

Each sample was subjected to the flame test for a period of 5 min. The thickness of each coating was measured before and after the fire test to determine the degree of intumescence.

### 3.7. X-ray diffraction analysis

Samples were heated from room temperature to 500 °C over an 8 h period. The intumesced samples were then ground and sifted through a 200 mesh sieve tray. The powdered samples were analysed using a Phillips X-ray diffractometer with  $\text{CuK}_\alpha$  radiation providing a wavelength of 0.154 16 nm.

## 4. Results and discussion

### 4.1. Thermal analysis

#### 4.1.1. Sodium/potassium silicate system

The TGA and DSC results for the sodium silicate/potassium silicate samples are shown in Fig. 1a and b, respectively. The first endothermic peak for 100% sodium silicate is quite sharp with a few smaller peaks in the 130 to 150 °C temperature range. The sharp peak indicates one predominant hydrate to be present in the silicate sample. This is in contrast to the 50% sodium silicate and 0% sodium silicate (i.e. 100% potassium silicate) samples which gave two nearly equal sized peaks with a number of smaller peaks in the 130 to 200 °C temperature range. The TGA curves all indicate a rapid weight loss in the 130 to 200 °C temperature range corresponding to the observed

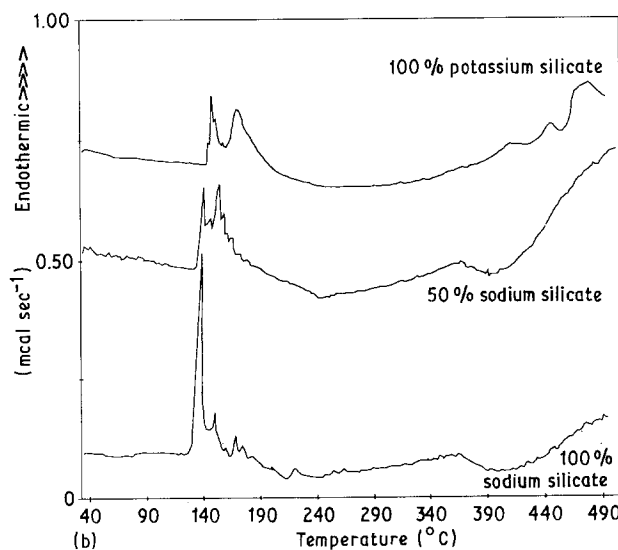
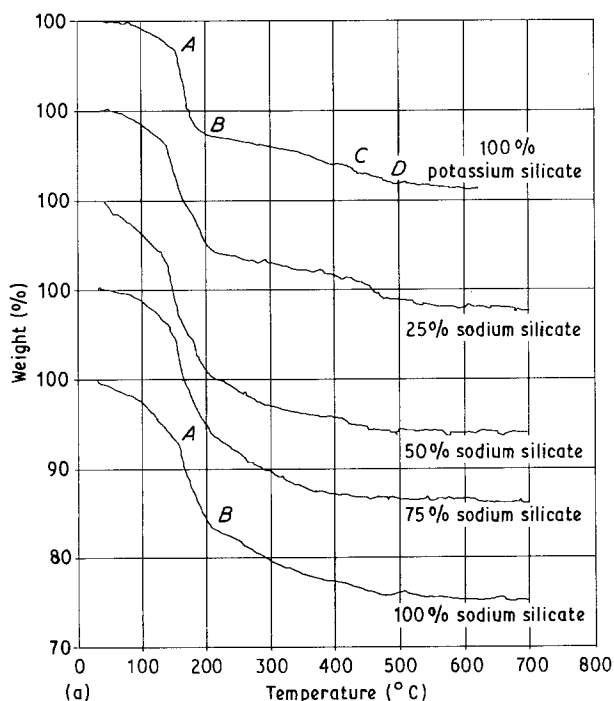


Figure 1 (a) TGA results and (b) DSC results for the sodium/potassium silicate system.

endotherms. This would correspond to a rapid evolution of water vapour providing the main driving force for the intumescence of the samples.

The 100% sodium silicate and 50% sodium silicate samples show broad endotherms in the 340 to 390 °C temperature range which probably correspond to strongly associated water molecules. However, the TGA results do not indicate a significant weight loss in this region and it must not involve a significant amount of water.

The 100% potassium silicate sample shows a definite endotherm in the 450 to 490 °C temperature range not evident in the 50% sodium silicate and 100% sodium silicate samples (the gradual rise in these curves in this temperature range is mainly due to baseline drift in the DSC instrument). This high temperature endotherm and weight loss (seen in the TGA results) probably corresponds to loss of structural water possibly from regions of  $\text{KHSi}_2\text{O}_5$  found to exist from previous work [10]. It should be noted that the conversion of polysilicate silanol groups to siloxane with the release of water, and the release of structural water, occurs by a similar mechanism, which is the dehydration of  $-\text{SiOH}$  groups. However, due to the irregularity of the polysilicate ions, this release of water occurs more gradually than the loss of structural water of a more highly ordered silicate species (i.e.  $\text{KHSi}_2\text{O}_5$ ) present within the polysilicate matrix. The dehydration of polysilicate silanol groups to siloxane groups will be a major factor at high temperatures (above 200 °C) in each of the samples and appears as a gradual weight loss superimposed on other forms of dehydration. The number of moles of water per mole of cation is shown in Table II. The endotherms in the 140 to 200 °C range correspond to about 1 mol water per mole of cation ( $\text{Na}^+$  or  $\text{K}^+$ ).

#### 4.1.2. Lithium/potassium silicate system

The TGA and DSC results for the lithium silicate/potassium silicate samples are shown in Fig. 2a and b, respectively. The samples with lithium concentrations of 50%, 75% and 100% all show low-temperature endotherms with maxima in the 70 to 80 °C range and with corresponding rapid weight losses in the TGA curves. This is absent in the 100% potassium silicate sample and can therefore be ascribed to lithium silicate hydrates. The peaks are quite broad and indicate

not a single anionic silicate species but water associated with the lithium cation in equilibrium with various anionic forms of the silicate ion, probably including higher order polysilicate ions. Calculations from the TGA curves indicate that 1.29 mol water per mole  $\text{Li}^+$  are lost in this temperature range for 100% lithium silicate (Table II).

The samples with 50% and 75% lithium silicate show broad endothermic peaks in the 120 to 190 °C range which are probably due to hydrates of potassium silicate because they are absent in the 100% lithium silicate sample but very pronounced in the 100% potassium silicate sample. The samples containing 50%, 75%, and 100% lithium silicate all show very broad and irregular endotherms in the 200 to 400 °C temperature range and this is also evident as a rapid weight loss in the TGA curves. This seems to indicate that part of the water associated with hydrates of the lithium cation and various silicate anions is strongly attached and given off in this temperature range. This would be analogous to lithium and sodium borates which release much of their water of hydration below 100 °C and the remainder in the 300 to 350 °C temperature range (e.g.  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ,  $\text{Li}_2\text{B}_{10}\text{O}_{16} \cdot 8\text{H}_2\text{O}$  [22]). This strongly attached water was calculated to be 0.57 mol per mole  $\text{Li}^+$  (Table II). The total bonded water, including water present as  $-\text{SiOH}$  was calculated to be 2.18 mol per mole  $\text{Li}^+$ .

The TGA and DSC results for samples containing 25% and 0% lithium (i.e. 100% potassium silicate) are quite similar. Both show large endotherms in the 140 to 190 °C and 420 to 500 °C temperature ranges with corresponding weight losses in the TGA curves. The endotherm in the 420 to 500 °C temperature range is ascribed to dehydration of  $\text{KHSi}_2\text{O}_5$  structural water.

#### 4.2. Cationic effect on water absorption

##### 4.2.1. Sodium/potassium silicate system

The water content versus relative humidity data are plotted in Fig. 3. From these data, the number of moles of water per mole of cation was calculated and is shown in Table III. At low relative humidity the values are in good agreement with the values found from thermal analysis (Table II) and indicates that at low relative humidity the water retained in the coating can be accounted for by ionic bonding (i.e. ionic hydration) and as structural water ( $-\text{SiOH}$  groups). It is believed that at high relative humidity, hydrogen bonding of water to surface silanol groups of polysilicate particles also plays a role in the absorption of water in the silicate matrix as is the case with silica gels.

The expansion of the silicate coatings on aluminium substrates (calculated on a per cent basis using the thickness at 5% r.h. as the datum) is shown in Fig. 4. The 100% sodium silicate sample showed significantly less expansion than the potassium silicate sample, even though it absorbed approximately the same amount of water between conditions of 5% and 95% r.h. This may be due to the stronger force of attraction for  $\text{Na}^+$  to negatively charged silicate anions than that

TABLE II Moles of water per mole of cation calculated from TGA

Silicate	Moles water/moles cation			Total
	Ionicly bonded $\text{H}_2\text{O}$	Ionicly bonded $\text{H}_2\text{O}$	$\text{H}_2\text{O}$ as $-\text{SiOH}$	
Li-silicate	1.29 <sup>a</sup>	0.57 <sup>b</sup>	0.32 <sup>c</sup>	2.18
K-silicate (88)	1.06 <sup>a</sup>		0.80 <sup>c</sup>	1.86
Na-silicate	0.94 <sup>a</sup>		0.83 <sup>c</sup>	1.77
K-silicate (6)	0.89 <sup>a</sup>		0.66 <sup>c</sup>	1.55

<sup>a</sup>Weight loss in region A-B. <sup>b</sup>Weight loss in region C-D. <sup>c</sup>Weight loss in region > A minus ionically bonded  $\text{H}_2\text{O}$ .

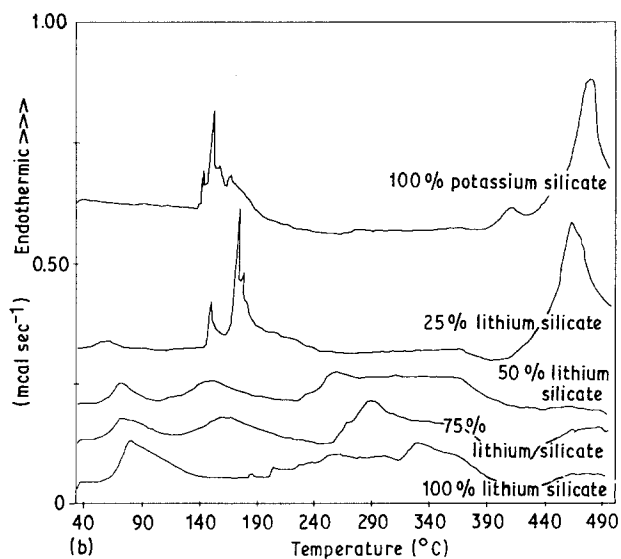
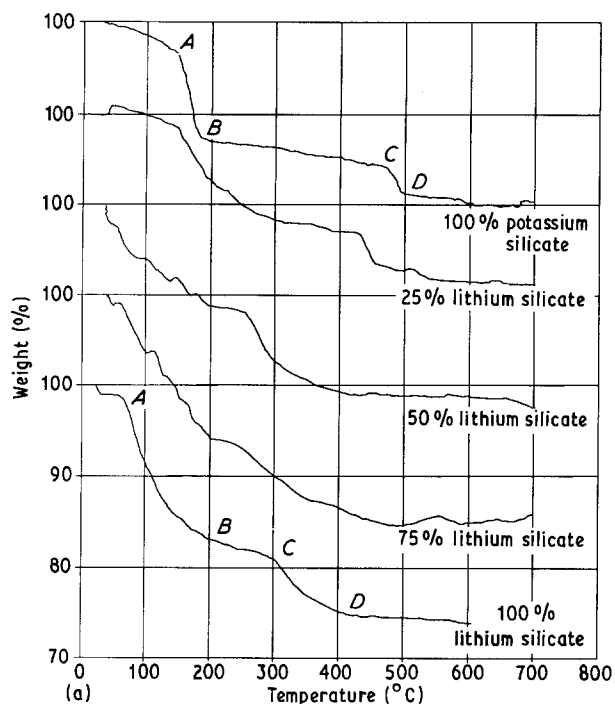


Figure 2 (a) TGA results and (b) DSC results for the lithium/potassium silicate system.

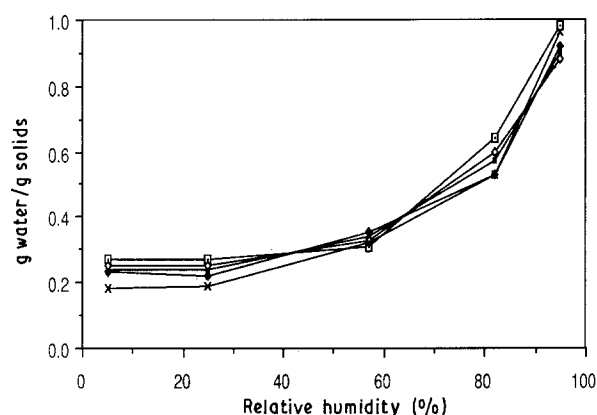


Figure 3 Water content versus relative humidity for the sodium/potassium silicate system (□) 100% Na, (◆) 75% Na: 25% K, (■) 50% Na: 50% K, (◇) 25% Na: 75% K, (×) 100% K.

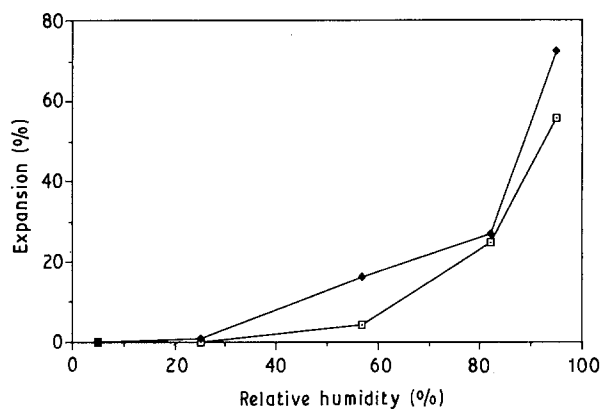


Figure 4 Expansion versus relative humidity for the sodium/potassium silicate system. (□) 100% Na, (◆) 100% K.

of  $K^+$ , as is evinced by the lower solubilities of sodium silicates than potassium silicates.

#### 4.2.2. Lithium/potassium silicate system

The water content versus relative humidity curves are shown in Fig. 5 for the lithium/potassium silicate system. It can be observed that the samples with 100%

and 75% lithium silicate adsorb little or no additional water above 5% r.h. This is directly correlated to the expansion versus relative humidity data plotted in Fig. 6. It appears that  $Li^+$  forms strong cross-links between polysilicate particles which are not easily dissociated, and this prevents the structure from expanding and allowing the adsorption of additional water. This agrees with work by Lawrence and Vivian

TABLE III Moles of water per mole of cation calculated from water retention versus relative humidity data

Sample	Moles water/moles cation				
	5% r.h.	25% r.h.	57% r.h.	82% r.h.	95% r.h.
Sodium silicate	2.03	2.00	2.27	4.69	7.08
Potassium silicate (6)	1.48	1.52	2.63	4.24	8.07
Lithium silicate	2.39	2.56	2.56	2.56	2.56
Potassium silicate (88)	2.66	2.83	3.93	5.43	8.79

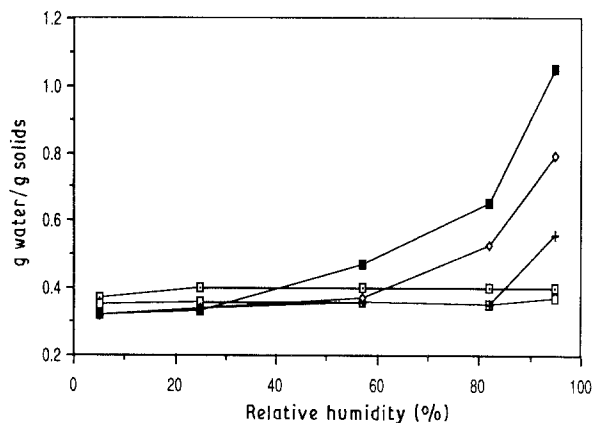


Figure 5 Water content versus relative humidity for the lithium/potassium silicate system. (□) 100% Li, (◇) 75% Li: 25% K, (+) 50% Li: 50% K, (■) 100% K.

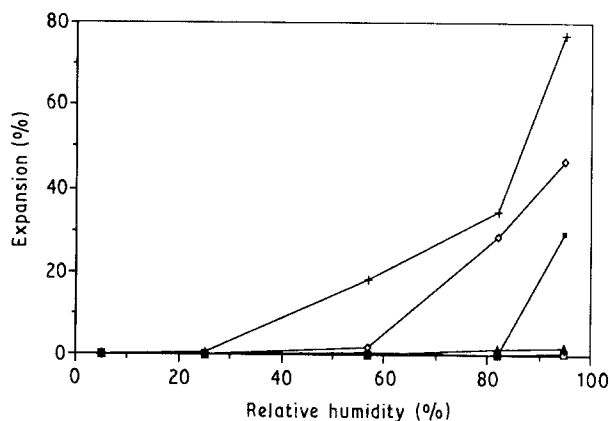


Figure 6 Expansion versus relative humidity for the lithium/potassium silicate system. (■) 100% Li, (▲) 75% Li: 25% K, (■) 50% Li: 50% K, (◇) 25% Li: 75% K, (+) 100% K.

[23] who observed that lithium, when added to mortar, showed significantly less expansion over time than sodium- and potassium-containing mortar.

Experiments showed that when 100% lithium silicate was allowed to room dry and then placed in a humidity chamber at 57% r.h. or higher, the samples would adsorb additional water and expand. Apparently, there is some minimum limit to which the lithium silicate coating can be dried below which it becomes irreversible to further hydration by increase in relative humidity. Comparing Tables II and III it can be seen that the water contained in the lithium silicate sample at 5% r.h. can be accounted for as strongly ionically hydrated and as  $-\text{SiOH}$  groups. This may correspond to a stable hydrate that does not readily dissociate as the relative humidity is increased. The room-dried sample may not have dried sufficiently to form this stable hydrate and was therefore able to absorb additional water as the relative humidity was increased.

#### 4.3. X-ray diffraction results

When samples were gradually heated (room temperature to 500 °C in 8 h) the diffraction patterns shown in Fig. 7 were obtained. No pattern was detected for sodium silicate. Potassium silicate, and 50% sodium

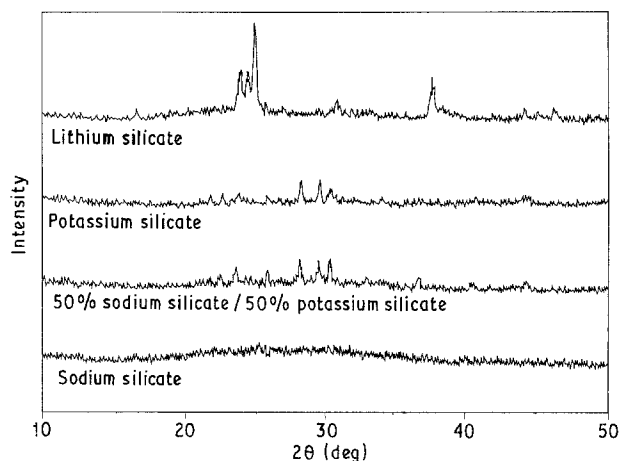


Figure 7 X-ray diffraction results.

silicate/50% potassium silicate samples produced a pattern corresponding to  $\text{KHSi}_2\text{O}_5$ . Lithium silicate showed a pattern corresponding to  $\text{Li}_2\text{Si}_2\text{O}_5$ . This forms a hydrate,  $\text{Li}_2\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ , which explains the release of water in two temperature ranges as observed in the TGA results. However, the signals are relatively noisy and the detected crystals likely are isolated in crystalline regions within the polysilicate matrix.

#### 4.4. Effect of the cation on the intumescence

##### 4.4.1. Sodium/potassium silicate system

Intumescence and solubility data for the sodium/potassium silicate system are plotted in Figs 8 and 9, respectively. The intumescence tests provided interesting results. It was found that a coating consisting of a mixture of potassium silicate and sodium silicate gave a higher degree of intumescence than either silicate alone. Even though 100% sodium silicate gave a relatively low degree of intumescence, adding even 25% potassium silicate increased the degree of intumescence by a factor of 2, and was greater than that of 100% potassium silicate. The reason for this is unclear.

The solubility data show some correlation with the intumescence data as do the expansion versus relative humidity data shown in Fig. 4. Comparing 100%

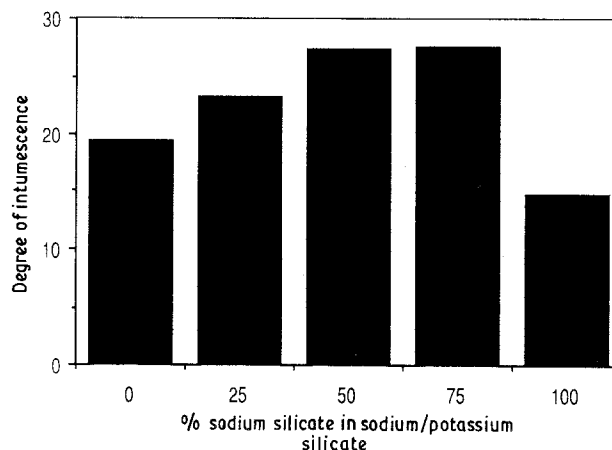


Figure 8 Degree of intumescence versus per cent sodium in sodium/potassium silicate system.

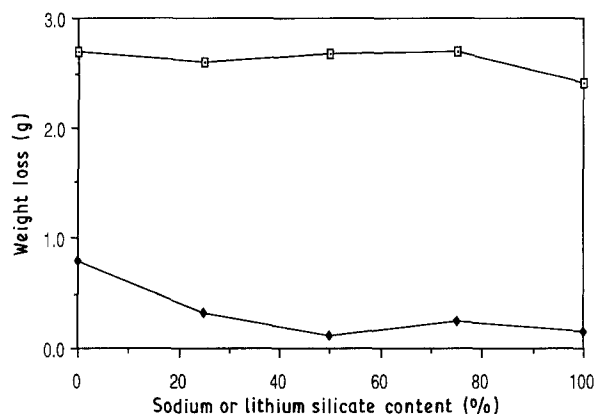


Figure 9 Solubility versus % cation ( $\text{Na}^+$  or  $\text{Li}^+$ ) in sodium/potassium silicate (3.3 molar ratio  $\text{SiO}_2:\text{K}_2\text{O}$ ) and lithium/potassium silicate (3.45 molar ratio).

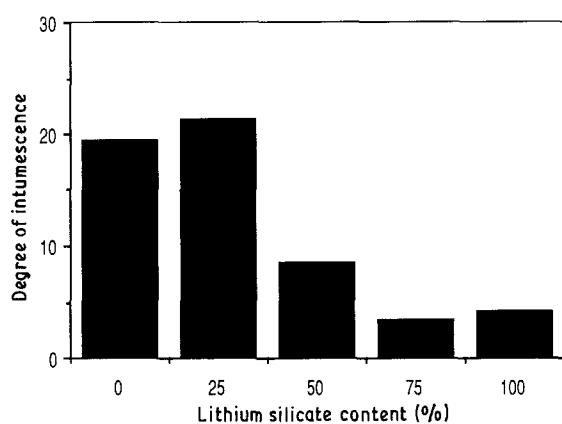


Figure 10 Degree of intumescence versus %  $\text{Li}^+$  in lithium/potassium silicate system.

sodium silicate with 100% potassium silicate in terms of the solubility, expansion, and intumescence data, it is evident that the strength of cationic cross-links between polysilicate particles is greater for  $\text{Na}^+$  than for  $\text{K}^+$ .

#### 4.4.2. Lithium/potassium silicate system

The degree of intumescence data and solubility data for the lithium/potassium silicate system are plotted in Figs 10 and 9, respectively. There is a definite correlation between intumescence, solubility, and expansion versus relative humidity (Fig. 6). Evidently, the  $\text{Li}^+$  cation forms much stronger cross-links between polysilicate particles than  $\text{K}^+$ .

## 5. Conclusions

Thermal analysis indicated that the loss of ionically hydrated water is the predominant mechanism of

dehydration and intumescence of the silicate-based samples tested. Loss of structural water is also a major factor in the dehydration.

The lithium ion forms strong cross-links between polysilicate particles which limit water adsorption due to the rigidity of the structure. This same mechanism reduces water solubility and degree of intumescence.

The degree of intumescence follows the pattern potassium silicate > sodium silicate > lithium silicate ( $\text{K}^+ > \text{Na}^+ > \text{Li}^+$ ): the smaller the cationic radius the lower the degree of intumescence and solubility. However, in the sodium/potassium system, a mixture of sodium silicate and potassium silicate provides a higher degree of intumescence than either separately.

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